(19) Patent Office of Japan (JP)(11) Publication of Patent Application: **Showa 50-25608**

(43) Publication: Showa 50 (1975) 3.18

Int. CL. 5	ID Code Office Cont'l No.	Japanese Classification
C 03 C 3/12	6730 41	20 (3) C12P
	7417 41	21 A2

Verification request: Not requested

Number of pages (total of 5 pages)

---

(21) Filed Number: Application Showa 48-75645

(22) Filed Date: Showa 48 (1973) 7.6

(71) Patent Assignee: (Toho) Research Institute Iron and Steel

JP 50-25608

[Note: Very poor copy of the original. Names, addresses, company names and brand names are translated in the most common manner. Japanese language does not have singular or plural words unless otherwise specified by a numeral prefix or a general form of plurality suffix.]

Description of the Invention

1. Name of the Invention

Manufacturing Method for High Melt Point Glass Body

2. Scope of the Claims

Manufacturing method for the preparation of high melt point glass body characterized by the fact that a sintered body from a mixed material that is an $Al_2O_3 - Ln_2O_3$ system (where Ln represents rare earth metal element and yttrium element), which is difficult to form a glass state, and which is formed as relative to the fine powder material of α-Al_2O_3, one type or two or more types of any Ln_2O_3 fine powder materials, are added, is heated at a temperature of approximately 2500oC or higher, and preferably at a temperature of 3000oC or higher using an arc plasma flame, and it is melted, and this is then rapidly cooled and a transparent to visible light beam ceramics glass body is obtained continuously.

3. Detailed Description of the Invention

The present invention is an invention about a large scale manufacturing method where a high melting point oxide material, which is difficult to form a glass state, and its system, are melted by using an arc plasma flame and this material is supplied in the gap between cooling rolls that are rotating at a high speed, and it is rapidly cooled and it becomes a material in a glass state, and a ceramic glass body that is transparent to visible light is obtained.

Among the many oxide compounds, as it is well known, as the components that easily form a glass state there are B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, etc. The present invention is an invention whereby relative to this, improves the rapid cooling methods used according to the previous technology relative to the oxide compounds and their systems, which are difficult to form a glass state, like for example, $Al_2O_3 - Ln_2O_3$ (where Ln represents rare earth metal element and yttrium element), and it uses an arc plasma flame and an impact quenching etc., high speed cooling method, and it realizes a new Al-Ln-O glass state.

Namely, it is an invention that suggests a manufacturing method for the preparation of a glass body from an $Al_2O_3 - Ln_2O_3$ system (where Ln represents rare earth metal

element and yttrium element), which has been said to be difficult to form a glass state according to the previous technology, and according to the present invention, first a sintered body which is formed as relative to the fine powder material of α-Al2O3, one type or two or more types of any Ln2O3 fine powder materials, are added, is heated at a temperature of approximately 2500oC or higher, and preferably at a temperature of 3000oC or higher using an arc plasma flame, and it is melted, and this is then rapidly cooled, for example by the method where it is supplied in the gap between cooling rolls rotating at a high speed, and a transparent to visible light beam ceramics glass body is obtained continuously.

Here below, an explanation will be provided relative to the manufacturing of Al2O3 – Ln2O3 system glass body.

Granulated below 325 mesh (45 microns), fine powder form, high melting point oxides of α-Al2O3 and Ln2O3 were mixed at different mole ratios, and sintered bodies with a cylindrical shape with dimensions of 3 mm diameter x 30 mm, were formed. This sintered bodies were placed in a chuck and their edges were melted by a two stand arc plasma flame and the molten material flowed in the gap between two rotating at a high speed rollers of an inner part cooling device and by that it was possible to produce a transparent to the visible light experimental material with a thickness of approximately 1 micron and a diameter of approximately 50 mm. Regarding the mole ratio of the α-Al2O3 and the Ln2O3 in this case, it is preferred that the ratio of the Ln2O3 relative to 1 mole of α-Al2O3 be within the range of 0.1 ~ 10 moles. Naturally, when both materials are used individually a glass body is not obtained. The fact whether or not the obtained by this method experimental material is a glass material was studied by using a polarized light microscope, an X- Ray diffraction and an electron microscope. According to the method using a polarized light microscope, the experimental material was placed in the space between orthogonal Nicol and an orthoscopic observation was conducted. For the experimental material, even if the stage was rotated, a change in the image contrast was not observed. Then, for the X ray diffraction image and for the electron beam diffraction image, only a halo image was observed. In the viewing filed by the electron microscope there was no intervening material observed. In Figure 1 the electron beam diffraction image (Figure 1 – 1) of the experimental material from the Al-Ln-O system and its planar viewing field image (Figure 1 – 2), are presented. The phenomenon of crystallization of the Al-Ln-O system experimental material by subjecting it to a thermal treatment at a temperature of 1000oC for different number of hours was studied by using X ray diffraction. The results from that are shown in Figure 2. From the above-described observations it is possible to determine that the experimental material obtained by using the above-described equipment is a glass material. Regarding such glass material, it is possible to obtain various compositions of the Al-Ln-O system, and the elements that are represented by the above described Ln are La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu and Y. Regarding the produced glass material, it is transparent relative to visible light, and also, regarding the Ln element, usually, the elements that are present in a third valency are stable, however, among the Al-Ln-O glass materials, the materials where Ln is Sm, Eu and Yb and these elements are present in a bivalent state, it is

considered that a coloration is developed. In Figure 3 the obtained glass material is presented.

The coloration of the obtained Ln-Al-O system glass is according to the described here below.

Ln-Al-O	Color
La-Al-O	colorless
Ce-Al-O	colorless
Pr-Al-O	pale green color
Nd-Al-O	pale blue color
Sm-Al-O	brown color
Eu-Al-O	pale yellow color
Gd-Al-O	colorless
Tb-Al-O	colorless
Dy-Al-O	colorless
Ho-Al-O	colorless
Er-Al-O	pale orange color
Tm-Al-O	colorless
Yb-Al-O	pale brown color
Lu-Al-O	colorless
Y-Al-O	colorless

Regarding the glass materials that is obtained by using the above described glass material manufacturing installation, and using an oxide material or its system that are difficult to form a glass state irrespective of the type of the used Al-Ln-O system, it is anticipated that they are materials that have properties that are different from those of the glass materials obtained according to the previous technology from glass, B_2O_3, SiO_2, etc., and it is considered that from the standpoint of the optical, electric and magnetic properties, they are materials that can play an extremely important role in the different aspects of the electronic memory related technologies and also in other processing technologies.

Practical Examples

The manufacturing of high melting point ceramic glass materials uses the equipment presented according to Figure 4. Here below an explanation will be provided by using the figure.

In the figure, 1 represents a chuck whereby in order to produce the glass material, the sintered body experimental material can be moved in the up and down direction within the diagram. Also, in the figure, 2 represents the sintered rod. The material used in order to obtain the glass material, is a material where less than 325 mesh dispersity, fine powder form α-Al_2O_3 and Ln_2O_3, for example, La_2O_3, powder are weighed at the

corresponding mole ratio, and after that these are well mixed and combined by using a mixing device, and this material is press molded in a cylindrical shape with dimensions of 3 mm diameter x 50 mm, and this cylinder shape material is sintered at a temperature of approximately 1000oC for a period of 20 hours in an air atmosphere. The cylinder shaped sintered material body 2 is grasped by the chuck 1 so that, as shown according to the presented in Figure 1, its front end is introduced into an arc plasma flame. 3 represents argon arc plasma flame (with a temperature of at or above approximately 3000oC), and it is at a temperature of approximately 2500oC or above, and preferably, it is at or above approximately 3000oC. 4 represents the arc plasma nozzle, 5 represents the roller where the inner part is cooled by water, and that rotates at 1000 rpm or higher, and where by the motion in the left and right direction, it is possible to adjust the thickness of the glass material. The molten material obtained from the sintered body enters in the gap between the two rollers that are rotating at a speed of approximately 1000 rpm, and from the rollers, a transparent glass material with a thickness of approximately 1 micron, is obtained. The obtained glass material has a diameter in the range of 50 ~ 100 mm. Moreover, the details of the cooling part are shown in Figure 5. 6 (in Figure 4) represents the experimental material controlling device, 7 represents the produced glass material. This glass material is collected in the receptacle tray 8.

In Figure 5, 9 represents the motor used for the rotation, 10 represents the entrance in the cooling part where the cooling part used cooling water is transported, 11 represents its exit opening. The cooling water enters through the above described opening 10 close to the roller inside part separation wall 12 and it cools the roller surface. The water that has a somewhat higher temperature is directed to exit through the exit opening 11 by 13, which is close to the axis part.

Moreover, in Figure 6, a schematic diagram is shown of the essential parts of the device generating the above described argon arc plasma. If we are to provide a simple description, through the protection gas nozzle 14, as a protective gas 15, for example, a mixed gas containing 93 volume % Ar and 7 volume % H2 is used. 16 represents the melt injection head, 17 represents the cooling water. 18 represents the plasma gas (Ar), 19 represents the a tungsten electrode (- electrode), 20 represents a high frequency wave, 21 represents the electric source for the pilot arc, 23 represents the electric source for the melt injection arc. 23 represents a switch, 24 represents an arc plasma flame, 25 represents a (+electrode).

After that, the glass material that is obtained by using this equipment is presented in Figure 3.

In the case of this glass material, it can obtained from all rare earth type elements and yttrium element (Y) and also, it can obtained from almost all the mole ratios of the α-Al2O3 and Ln2O3, however, it is preferred that relative to 1 mole of the α-Al2O3, the amount of the Ln2O3 is within the range of 0.1 ~ 10 moles. The confirmation of the glass state of the material was conducted by using polarized light microscope, X ray diffraction and electron beam diffraction.

In the above described Figure 1, the electron beam diffraction pattern and the microscopic image of the glass material obtained as $Al2O3$: $Ln2O3$ = 6:1 are weighed, as a representative example of the Al-Ln-O system, are shown. For the electron microscope a manufactured by Nippon Denko Company, 200 kV microscope, was used. Regarding the electron beam diffraction image, it was projected at an acceleration electric potential of 150 kV, and it showed a typical halo image. The fact that this halo image was obtained indicates that the obtained experimental material is a glass material. Regarding the electron microscopic image, it is an image obtained by a bright viewing field image at a magnification of 62,000 times. From this image it is seen that there are no intervening materials present at all and this indicates that the obtained glass material is a microscopically good glass material. Then, by the observation through a polarized light microscope, it is confirmed that even when the experimental material is rotated, there is no change in the contrast at all, and this indicates that macroscopically also it is a good glass material. Also, in Figure 2, the results are shown from a measurement conducted by an X-ray diffractometer using CuKα relative to the manufactured glass material after it has been subjected to a thermal treatment for the time period as shown in the figure, and this studies the conditions of the crystallization.

As it has been described here above, according to the present invention it is possible to suggest a manufacturing method for the preparation of high melt point glass body characterized by the fact that a sintered body from a mixed material that is an Al2O3 – Ln2O3 system (where Ln represents rare earth metal element and yttrium element), which is difficult to form a glass state, and which is formed as relative to the fine powder material of α-Al2O3, one type or two or more types of any Ln2O3 fine powder materials, are added, is heated at a temperature of approximately 2500oC or higher, and preferably at a temperature of 3000oC or higher using an arc plasma flame, and it is melted, and this is then rapidly cooled by using for example a method where this molten material is rapidly cooled in the space between rotating at a high speed cooling rollers and a transparent to visible light beam ceramics glass body is obtained continuously.

Here above, mainly, a practical example was described where La2O3 was used as the Ln2O3, and also, as the rapid cooling method for the material that has been melted by the argon arc plasma, water cooled type, high-speed rotating rollers were used, however, after this, as other practical example, there is the example where Nd2O3 was used as the Ln2O3, and where for the rapid cooling method, the equipment shown according to Figure 7, that has a structure formed from a water cooled piston 26 and an anvil 27, was used.

Regarding the α-Al2O3 and Nd2O3 that are used as the material, they are both materials where the purity level is at least 99.9 % or higher, and also, they are materials that are in a fine powder form. The mole ratio of both materials, namely, α-Al2O3:Nd2O3 = x : 1, where x was within the range of 1 and 10. Both materials were well pulverized, mixed and combined, and they were subjected to an elevated pressure of 4 ton/cm2, and pellets with a thickness of 1 mm and a diameter of 5 mm, were formed. These pellets were sintered in an air atmosphere at a temperature of 1000oC for a period of 5 hours. The pellets 28 of this sintered experimental material were placed inside a manufactured from

Cu piston, as shown according to Figure 7, and they were melted by the plasma flame 25 until the experimental material formed a spherical shape. While heating by using the plasma flame 25, the water cooled by the cooling water 30 piston 26 and the manufactured from copper anvil 27 are operated by the spring 31 and the electro-magnet (not shown in the figure), and the molten material is enclosed in the space between the two and it is rapidly cooled. Moreover, in this case, the above described plasma flame 25 is discharged from the plasma torch 32.

Regarding the produced glass material, at a diameter of approximately 5 mm and a thickness of approximately 1 micron, it is a material that is transparent to visible light beam. The glass material obtained from the α-Al2O3 : Nd2O3 = 6 : 1 experimental material was subjected to a an orthoscopic observation by the polarized light microscopic method, in the space between orthogonal Nicol, and the same way as in the above described practical example, even if the stage was rotated, there was no change in the image contrast. Then, through the X ray diffraction pattern, and the electron beam diffraction image, only a halo pattern was observed. Then, when using an electron microscope, in the bright viewing field image there were no intervening materials observed. Figure 8 is a diagram presenting the results from the X ray diffraction studies of the crystallization phenomenon in the case when the above described Al-Nd-O system experimental material was annealed at a temperature of 1000oC for different number of hours (CuKα radiation, (using Ni filter), pulse height analysis).

From the above described it is confirmed that the isotropic properties possessing materials that are obtained from the 6α-Al2O3. Nd2O3 obtained from each of the above described experimental materials, are glass materials.

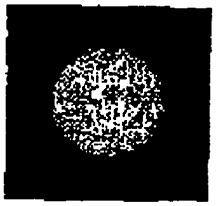
4. Brief Explanation of the Figures

Figure 1-1 represents the electron beam diffraction pattern (150 kV) of the Al-La-O type glass material; Figure 1-2 represents its bright viewing field pattern (x 62500); Figure 2 represents the results from the measurement of the crystallization of the Al-La-O type glass by the X ray diffraction method. Figure 3 represents a photograph of a thin piece of the Al-Ln-O type glass material. Figure 4 represents the glass material manufacturing equipment according to the first practical example of the present invention. Figure 5 represents a front view diagram where one part of the inner part of the cooling roller 5 from Figure 4, has been cut open. Figure 6 represents a schematic diagram showing the essential parts of the argon arc plasma generating equipment according to the present invention. Figure 7 is a glass manufacturing equipment related to another practical implementation example according to the present invention. Figure 8 is a line chart diagram showing the results from the X ray diffraction measurements of the crystallization of the same Al-Nd-O type glass.

1........................chuck for the sintered body of the experimental material,
2..................sintered rod, 3.......................argon arc plasma flame,
4.....................arc plasma nozzle, 5......................cooling roller,
6.........................experimental material controlling device,

7....................synthesized glass material, 8.........................glass material receptacle tray, 9..................motor, 10.........................cooling water entrance opening, 11.....................cooling water exit opening, 12................................inner part perimeter vicinity, 13..................inner part axis vicinity, 14.......................protective gas nozzle, 15.........................protective gas, 16....................................discharge head, 17......................cooling water, 18............................plasma gas (Ar), 19...........................tungsten electrode (- electrode), 20............................high frequency, 21...................electric source for the pilot arc, 22......................electric source for the melt radiation arc, 23.....................switch, 24.....................arc plasma flame, 25..................roller (+ electrode), 26.........................piston, 27..........................anvil, 28.................pellets, 29...................plasma flame, 30.......................cooling water, 31..................spring, 32........................plasma torch.

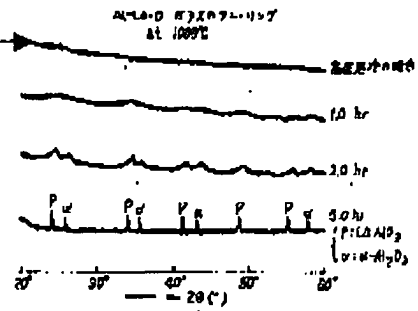
第1図−1



第1図−2

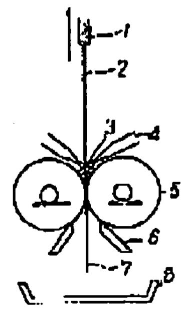
第2図

In the case of high frequency

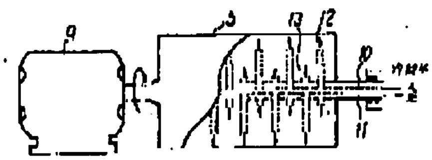


第3図

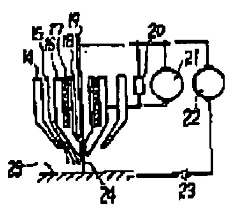
第4図



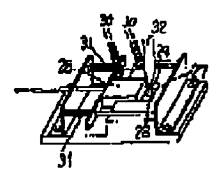
第5図



第6図



第7図



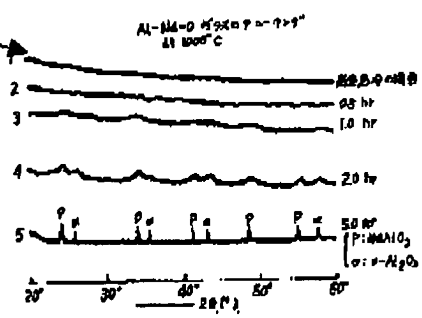
5. 添付書類の目録

6. 前記以外の発明者、特許出願人または代理人

(1) 発明者

第8図

In the case of high frequency



(2) 代理人

5. Record of the Appended documents

(1) Description	1 copy
(2) Figures	1 copy
(3) Application copy	1 original
(4) Power of attorney	1 copy

6. Other than the above described invention authors, patent applicants or representatives

Patent Assignee: (Toho) Research Institute Iron and Steel

Translated by Albena Blagev ((651) 735-1461 (h), (651) 704-7946 (w))

12/07/04

収入
審査不要

特許願

昭和48年7月6日

特許庁長官 三宅幸夫 殿

1. 発明の名称
高融点セラミックスのガラス体の製造方法

2. 発明者
茨城県東茨城郡大洗町大貫町
矢島
(ほか名)

3. 特許出願人
宮城県仙台市片平2丁目1番1号
東北大学金属材料研究所長
代表者 竹内 栄

特許庁 48.7.6 出願第二課

4. 代理人
住所 東京都千代田区霞が関3丁目2番4号 郵便番号100
霞山ビルディング7階 電話(581)2241番(代表)
(5925) 氏名 弁理士 杉村暁秀
(ほか1名)

⑲日本国特許庁
公開特許公報
⑪特開昭 50-25608
㊸公開日 昭50.(1975) 3. 18
㉑特願昭 48-75685
㉒出願日 昭48.(1973) 7. 6
審査請求 未請求 (全5頁)
庁内整理番号
6730 41
7417 41
(52)日本分類
20(3)C12?
21 A2
(51)Int.Cl².
C03C 3/12

明細書

1. 発明の名称　高融点セラミックスのガラス体の製造方法

2. 特許請求の範囲

ガラス状態になりにくいAl_2O_3-Ln_2O_3系（但しLnは稀土類元素およびイットリウム元素を示す）の高融点酸化物において微粉状α-Al_2O_3に対しLn_2O_3の何れか1種又は2種以上から成る微粉末を加えて成る混合物の焼結体をアークプラズマフレームにて約2500℃以上好ましくは約3000℃以上に加熱溶融せしめ、これを高速急冷せしめ可視光線にて透明なセラミックスガラス体を連続的に得ることを特徴とする高融点セラミックスのガラス体の製造方法。

3. 発明の詳細な説明

本発明はガラス状態になりにくい高融点酸化物及びその系をアークプラズマフレームにより溶融し、之を高速回転する冷却ロール間に供給し、高速急冷してガラス状態にし、可視光線に対して透明なセラミックスガラス体を大量に製造する方法に関するものである。

多くの酸化物の中でガラス状態になりやすい骨格成分は、周知のようにB_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5等である。本発明はこれに反し従来からガラス状態になり難いとされていた酸化物及びその系、例えばAl_2O_3-Ln_2O_3系（Lnは稀土類元素群およびイットリウム元素をさす）を、従来の急冷方法を改良し、アークプラズマフレームとインパクトクエンチング等の超急冷法を使用して、初めてAl-Ln-O系のガラス状態を実現しようとするものである。

すなわち、従来からガラス状態になりにくいと称せられていたAl_2O_3-Ln_2O_3系（ここでLnは稀土類元素およびイットリウム元素を示す）のガラス体の製造方法を提供しようとするものであり、本発明では先ず、微粉状α-Al_2O_3に対しLn_2O_3の何れか1種又は2種以上の微粉末を加えてなる混合物の焼結体をアークプラズマフレームにて約2500℃以上好ましくは約3000℃以上に加熱溶融せしめ、これを例えば高速回転冷却ロール間にて

急冷せしめる如き高速急冷方法によつて急冷せしめ、可視光線にて透明なセラミツクスガラス体を短時間に得られるようにしたものである。

以下 Al_2O_3 − Ln_2O_3 系のガラス体製造に関する説明を行なう。

325メツシユ(44μm)以下の粒度にした微粉状高融点酸化物 α-Al_2O_3 および Ln_2O_3 を各種のモル比に混合し、3mmφ×30mmの円柱状の焼結体にした。この焼結体をチヤツクで吊るし、その先端を2台のアークプラズマフレームで溶解し、溶融物を内部冷却装置のついた高速回転している2台のローラーの間に流しこむことによつて約1mmの厚さを有し直径約30mmの可視光線に対して透明な試料を作成することができた。この場合のα-アルミナ(Al_2O_3)と Ln_2O_3 とのモル比は、Al_2O_3 1モルに対し Ln_2O_3 0.1〜10モルが好適である。勿論両者の純粋の単味ではガラス体は得られていない。このようにして得られた試料がガラス体であるかどうかは偏光顕微鏡、X線回折及び電子顕微鏡によつて調べた。偏光顕微鏡を用いる方法では直交ニコル間に試料を置き、オルソスコープ観察を行なつた。試料のおいてあるステージを回転しても像のコントラストに変化は観察されなかつた。さらにX線回折像、電子線回折像ではハロー像しか観察できなかつた。電子顕微鏡による明視野像では介在物は観察されなかつた。第1図にAl-La-O系における試料の電子線回折像(第1図−1)及びその明視野像(第1図−2)を示す。Al-La-O系の試料を1000℃でいろいろな時間熱処理することによつて結晶化する現象をX線回折で調べた。その結果を第2図に示す。以上の観察事実より上記の装置で得られた試料はガラス体であることが同定された。このようなガラス体はAl-Ln-O系のあらゆる組成のところで得られた。前記Lnで示す元素はLa, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu及びYである。作成したガラス体は可視光線に対して透明であり、又Ln元素は一般には3価で存在するのが安定であるがAl-Ln-O系ガラス体の中でLnがSm, Eu, 及びYbではそれらの元素が2価で存在していると思われる色彩を呈している。第3図に得られたガラス体を示す。

得られたLn-Al-O系の透明なガラスの色彩は次の如くであつた。

Ln-Al-O	色
La-Al-O	無色
Ce-Al-O	無色
Pr-Al-O	薄い緑色
Nd-Al-O	薄い青色
Sm-Al-O	橙色
Eu-Al-O	淡黄色
Gd-Al-O	無色
Tb-Al-O	無色
Dy-Al-O	無色
Ho-Al-O	無色
Er-Al-O	薄い桃色
Tm-Al-O	無色
Yb-Al-O	薄い褐色
Lu-Al-O	無色
Y-Al-O	無色

上記のガラス体製造装置を使用してAl−Ln−O系のみならずガラス状態になり難い酸化物及びその系において得られるガラス体は従来のガラス、B_2O_3, SiO_2 等の系よりなるガラスとは異なつた性質を持つことが予想され、光学的、電気的、磁気的性質の立場から記憶素子関係其の他工業的に各方面で非常に役立つものと思われる。

実施例

高融点セラミツクスのガラス体製造は第4図に示す装置を使用する。以下図面を用いて説明を行なう。

1はガラス体を作成する為の焼結体試料チヤツクで図中で上下に動作できる。2は焼結棒を示す。ガラス体を得る為の試料は、325メツシユ以下の粒度にした微粉状α-アルミナと Ln_2O_3 例えば La_2O_3 の粉末を適当なモル比に秤量した後、攪拌機でよく混合し3mmφ×30mmの円柱状にプレス成形した。この円柱状物質を約1000℃で20時間大気中で焼結したものである。円柱状焼結体2を第4図に示すようなチヤツク1に挟み、先端がアルゴンアー

クプラズマフレームの中に入るように設置する。3はアルゴンアークプラズマフレーム（約3000℃以上の温度）を示し、約2500℃以上、好ましくは約3000℃以上である。4はアークプラズマノズルを示す、5は水で内部冷却してあるローラを示し、1000 rpm以上で回転し、左右に移動することによつてガラス体の厚さを調整できる。融解体が溶融した瞬間約1000 rpmの速さで回転している2台のローラーの間に入りローラーからは約1μの厚さを持つ透明なガラス体が得られた。得られたガラス体は直径約6〜100 mmφの大きさを有している。

なお、冷却部の詳細については第3図に示す。6は試料のかきとり器を示し7は作成したガラス体を示す。これをガラス体の受台8によつて受ける。

第3図の9は回転駆動用モーターを示し、10は冷却部分に冷却部分へ冷却水を送る入口を、11はその出口を示す。冷却水は前記入口10から入りローラー内部の周壁近く12に入りロール表面を冷却する。若干温度の上つた水を前記の如く13から出口11へ出す。

なお、第6図に前記のアルゴンアークプラズマ発生装置の要部の模式図を示す。簡単に説明すると、14は保護ガスノズルで、保護ガス15としては、例えば、Ar 93容量%、H_2 7容量%の混合ガスを使用する。16は溶射ヘッドであり、17はその冷却水である。18はプラズマガス（Ar）、19はタングステン電極（一電極）、20は高周波、21がパイロットアークのための電源、22が溶射アークのための電源を示す。23はスイッチ、24はアークプラズマフレーム、25はローラ（＋電極）を示す。

次にこの装置を用いて得られたガラス体は第3図に示してある。

このガラス体は稀土類元素のすべておよびイットリウム元素（Y）で得られ、またα-Al_2O_3とLn_2O_3の殆んどすべてのモル比のところで得られ、好ましくはα-Al_2O_3 1モルに対しLn_2O_3 0.1〜10モルである。ガラス体であることの同定は偏光顕微鏡、X線回折、電子線回折によつて行なつた。

前記第1図にはAl-La-O系の典型的な例としてAl_2O_3：La_2O_3＝6：1に秤量して得られたガラス体の電子線回折像および顕微鏡像が示してある。使用した電子顕微鏡は日本電子社製の200 KVのものである。電子線回折像は加速電圧130 KVで撮影し、典型的なハロー像を示している。このハロー像から得られた試料がガラス体であることを示している。電子顕微鏡像は明視野像で62,500倍のものである。この像からこのガラス体には全く介在物が存在せず微視的に均質のガラス体であることを示している。さらに偏光顕微鏡による観察で試料を回転してもコントラストに変化が全くないことから巨視的にも均質のガラス体であることを示している。また、第2図には、製造したガラス体を図に示すような昇温熱処理した後、CuKα線によるX線ディフラクトメーターによつて測定した結果であり、結晶化の様子を調べたものである。

以上述べたように、本発明によれば、ガラス状態になりにくいAl_2O_3-Ln_2O_3系（但しLnは稀土類元素およびイットリウム元素（Y）を示す）の高融点酸化物において微粉状α-Al_2O_3に対しLn_2O_3の何れか1種又は2種以上から成る微粉末を加えて成る混合物の微粉体をアークプラズマフレームにて約2500℃以上好ましくは約3000℃以上に加熱溶融せしめ、これを高速回転冷却ロール間にて急冷せしめる等の急冷方法を用いることによつて、可視光領域にて透明なセラミックスガラス体を工業的に得る高融点セラミックスのガラス体の製造方法を提供することができる。

以上主としてLn_2O_3としてLa_2O_3を取り上げ、かつアルゴンアークプラズマによる溶融体の急冷方法として、水冷式高速回転ローターを採用した実施例について述べたが、次にさらに他の実施例としてLn_2O_3としてNd_2O_3を用い、急冷方法として第9図に示す如き水冷されたピストン26とかなとこ（アンビル）27とから構成された装置を採用した。

原料として用いるα-Al_2O_3およびNd_2O_3は共に純度として99.9%以上のものであり、また微粉末を用いる。両者のモル比、すなわちAl_2O_3：

$Nd_2O_3 - x : 1$ で x は 1 と 10 の間の範囲にある。両者をよく粉砕混合し 5 ton/cm² に加圧し、厚さ 1 mm 直径 5 mm のペレツトを成形する。このペレツトを空気中にて 1000℃ で 5 時間焼結する。この焼結された試料のペレツト 28 を第 7 図に示す Cu 製のピストン 26 の中に置き、試料が球状になるまでプラズマフレーム 24 によつて溶融される。プラズマフレーム 24 によつて加熱されながら冷却水 30 によつて水冷されるピストン 26 と銅製のかなとこ（アンビル）27 とをスプリング 31 と電磁石（図示せず）で作動させ、両者の間に挟んで溶融試料を急速に冷却させる。なお この場合前記プラズマフレーム 24 はプラズマトーチ 32 から放出される。

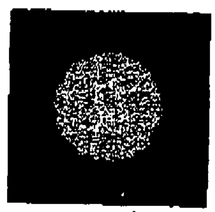
作成したガラス体は直径約 8 mm、厚さ約 1 μ で可視光線で透明である。$Al_2O_3 : Nd_2O_3 = 6 : 1$ の試料について得られたガラス体を偏光顕微鏡の方法で直交ニコル間にてオルソスコープ観察を行つた処、前記実施例におけると同様にステージを回転しても像のコントラストに変化はなかつた。さらにX線回折像、電子線回折像ではハロー像しか観察できなかつた。さらに電子顕微鏡による明視野像では介在物は観察されなかつた。第 8 図は前記の Al−Nd−O 系の試料ガラス体を 1000 ℃で各々の時間アニーリングすることによつて結晶化する現象をX線回折で調べた結果である（CuKα 放射（Ni フイルター）使用、パルスの高さの分析）。以上の各試験から $6Al_2O_3 \cdot Nd_2O_3$ から得られた等方性材料はガラス体であることが同定された。

4 図面の簡単な説明

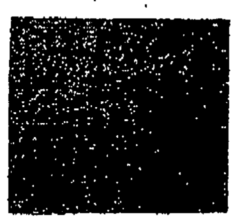
第 1 図−1 は Al−La−O 系ガラス体の電子線回折像（120 KV）、第 1 図−2 はその明視野像（×62500）、第 2 図は Al−La−O 系ガラスの結晶化のX線回折法による測定結果、第 3 図は Al−La−O 系ガラスの薄片の写真、第 4 図は本発明の一実施例に係るガラス体製造装置、第 5 図は第 4 図の冷却ローラー 5 の内部を一部切開して示す正面図、第 6 図は本発明に係るアルゴンアークプラズマ発生装置の概略を示す模式図、第 7 図は本発明の他の実施例に係るガラス体製造装置、第 8 図は同じく Al−Nd−O 系ガラスの結晶化のX線回折法による測定結果を示す線図である。

1…焼結体試料チヤツク、2…焼結棒、3…アルゴンアークプラズマフレーム、4…アークプラズマノズル、5…冷却ローラ、6…試料かきとり部、7…生成ガラス体、8…ガラス体受台、9…モーター、10…冷却水入口、11…冷却水出口、12…内部間隙附近、13…内部軸部附近、14…保護ガスノズル、15…保護ガス、16…溶射ヘツド、17…冷却水、18…プラズマガス（Ar）、19…タングステン電極（一極）、20…高周波、21…パイロツトアークのための電源、22…溶射アークのための電源、23…スイツチ、24…アークプラズマフレーム、25…ローラ（＋電極）、26…ピストン、27…かなとこ（アンビル）、28…ペレツト、29…プラズマフレーム、30…冷却水、31…スプリング、32…プラズマトーチ。

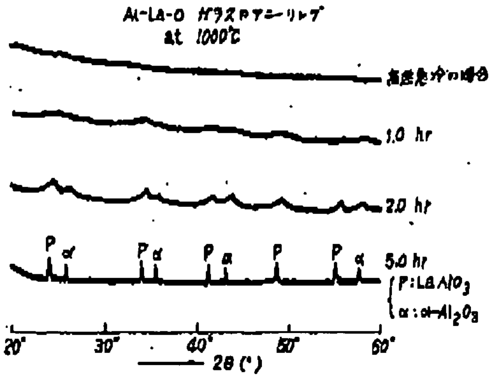
第1図−1



第1図−2

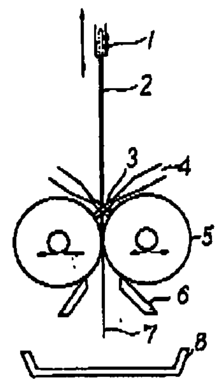


第2図

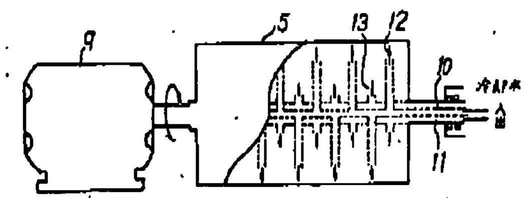


第3図

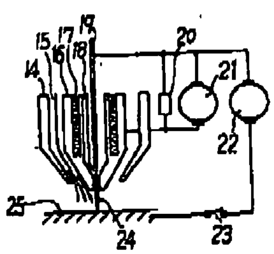
第4図



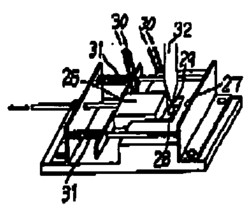
第5図



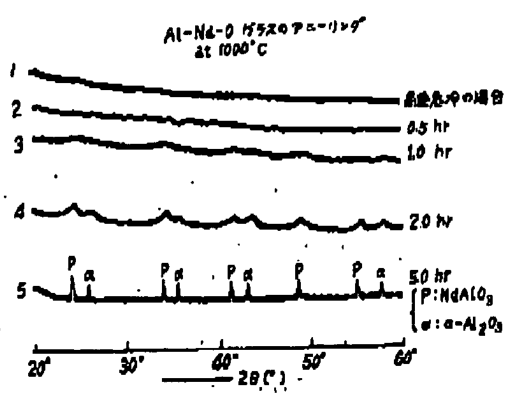
第6図



第7図



第8図



5. 添附書類の目録

(1) 明細書 1通
(2) 図面 1通
(3) 願書副本 1通
(4) 委任状 1通

6. 前記以外の発明者，特許出願人または代理人

(1) 発明者

住所 茨城県東茨城郡大洗町大貫町[illegible]番地

氏名 岡村 [illegible] 人

同上

氏名 宍戸 [illegible]

(2) 代理人

住所 東京都千代田区霞が関3丁目2番4号
郵便番号100
霞山ビルディング7階 電話(581)2241番(代表)

(7205) 氏名 弁理士 杉村興作